CHARACTERIZATION OF CONCRETES FORMULATED WITH BLENDS OF PORTLAND CEMENT AND OIL SHALE COMBUSTION ASH

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ABSTRACT

Previous experimental studies of the use of oil shale combustion fly ash in Portland cements have been reported by Germany, Israel, China, Jordan and the United States. In the current study seventeen samples of a standard concrete mix (49% coarse aggregate, 30% fine aggregate, 13% cement and 8% water) were prepared, containing various percent substitutions of Portland cement with oil shale fly ash from the pilot combustor of Occidental Oil Shale Company and commercial additives, and tested for unconfined compressive strengths. An increase in strength, consistent with observations in Israel and China, was found with substitution at 15%. Four standard mechanical tests were carried out preliminarily with the formulation with 45% substitution and a commercial additive, which gave a 90-day compressive strength of 5310 PSI. The freeze-thaw tests were confounded by poor coarse aggregate performance. The samples containing oil shale ash had less resistance to scaling than those containing no ash. Three zero-slump materials containing oil shale ash were investigated, again preliminarily. Three samples of compressed/autoclaved ash/lime paste ranged up to 2870 PSI. One of two samples of concrete masonry unit reached 1590 PSI. A sample of light-weight concrete, containing 40% fly ash, set up quickly, was hard and strippable in one day and had a density of 40 lb/ft^3.

INTRODUCTION

As a portion of a broader study of the beneficial use of ash from the combustion of oil shale from deposits owned by the Occidental Oil Shale Company in the western United States, the replacement of portions of Portland cement in standard concrete and of fine aggregate in zero-slump formulations by fly ash from a pilot plant combustor were evaluated at the University of Pittsburgh. Elements of this portion of the study include:

- a literature survey, identifying similar studies that have been carried out in several other countries, particularly in Israel and China;
- production of seventeen batches of concrete, containing oil shale combustion fly ash, and the measurement of the compressive strength of each over time;
- determination of two mechanical properties of a particular concrete, produced by one of the better formulations;

- a preliminary evaluation of zero-slump products containing oil shale combustion fly ash, specifically the preparation and examination of three samples formulated as brick, two samples as concrete masonry units and one sample as light-weight concrete.

LITERATURE

Previous experimental studies of the use of oil shale ash in cements have been carried out in the Federal Republic of Germany, the United States, Israel, China, the (former) USSR and Jordan. The work in the FRG and in the USSR has been reported only in German [1-6] and Russian [7-9], respectively. A review article by the Israelis [10] provides an excellent and comprehensive description of work in that country, as well as of the work in the Federal Republic of Germany and the United States. Four papers describing the Chinese work in English [11-14] are rather extensive, but they can be found only in a publication with, unfortunately, very limited circulation. The Jordanian paper is easily available and very informative [15].

ASH PROPERTIES

Three samples of fly ash from the Occidental Oil Shale pilot combustor were used in this study. The combustion temperature and percentages of shale and coal being fed to the pilot unit during the period of collection of each sample were:

Sample Period	Temperature (°F)	% Shale	% Coal
3	1550	54	46
4	1594	54	46
6	1500	65	35

Samples of the fly ash from Sample Periods 3 and 4 were analyzed by the Coal By-Products Utilization Laboratory (CBUL) of the ND Mining and Mineral Resources Research Institute at the University of North Dakota. Elemental compositions and LOI (Loss on Ignition) of these two samples, which relate to those found for other ashes were:

	SOURCE OF OIL SHALE ASH					
Comp.	FRG[10]	Israel[10]	China[12]*	Jordan[15]	Samp. 3	Samp. 4
CaO	16-60%	44.5	1.29	39.7	18.4	17.4
SiO_2	12.25	19.0	60.64	35.4	50.4	45.2
Al_2O_3	9-12	8.3	20.09	3.8	12.6	10.9
Fe_2O_3	6-7	4.3	11.89	2.0	4.6	4.5
MgO	1.4-2.0	0.7	0.83	4.0	6.6	6.6
SO_3	9-10	8.5	0.61	4.0	7.47	6.59
L.O.I.		11.3	0.55	7.3	0.38	0.24

* 860°C ash

The relatively high magnesia content of the fly ash from Sample Periods 3 and 4 does not appear to be a cause for concern. It is likely present in a bound form inside the ash particles. This is strongly suggested by CBUL's results, which determined that the expansiveness of the fly ash was almost an order of magnitude lower then the ASTM C618 Specification for both Class C and Class F fly ash.

CBUL also reported particle size distributions for which between 78 and 87 percent passed a #325 sieve. The fly ash thus meets the ASTM C618 Specification that at least 66 percent must pass this sieve to be a Class C or Class F fly ash.

CONCRETE FORMULATION AND COMPRESSIVE STRENGTHS

The basic concrete formulation used for seventeen test batches of ash-containing concrete, made during this study, was a standard mix of:

- 49 percent coarse aggregate;
- 30 percent fine aggregate;
- 13 percent Type 1 Portland cement;
- approximately 8 percent water.

[All formulation percentages throughout this paper are on a weight basis.] The water content was adjusted to provide a slump of two inches. Six batches also contained a workability (water-reduction) additive. Two of these six batches also used Type 3 Portland cement in place of Type 1 Portland cement.

Several trends were noted from a comparison of the 3-day, 7-day, 14-day and 28-day compressive strengths of cylinders (6 inches in length and 3 inches in diameter) formed from these seventeen batches. At low levels of Portland cement replacement (15 percent), oil shale fly ash behaves as a workability (or water reduction) agent and leads to a 9 percent higher compressive strength than that of standard concrete. This enhancement is lost by 30 percent replacement, which leads to a 9 percent lower compressive strength than that of standard concrete. The addition of the workability agent restores the high strengths, even at 45 percent replacement where it leads to a 9 percent higher compressive strength than that of standard concrete. Type 3 Portland cement does not appear to be effective in building compressive strength.

It is difficult to make direct comparisons to the work of other investigators because of differences in methodologies. The Germans, for example, make a special "oil shale cement" containing 27 percent oil shale ash and 73 percent Portland cement. It has compressive strengths up to 8800 PSI (60.8 MPa) at 28 days [10]. The Israelis make and compare pastes of Portland cement and oil shale. Portland cement pastes (water to cement ratios of 0.3 to 0.6) at 20 days reach 10,660 PSI (73.5 MPa), while oil shale ash pastes reach only 2830 PSI (19.5 MPa), when it has a water to cement ratio of 0.8 to 1.0 (which gives it the same consistency as the Portland cement paste). However, in making cement blends (Portland and oil shale ash together), the Israelis found that Portland cement replacement by 15 to 25 percent oil shale ash yielded concrete with slightly increased strength [10]. The Chinese report 28-day strengths as high as 11,200 PSI (77 MPa) with ash/Portland cement blends. They also found an increase in strength at replacements up to 25 percent [14]. The Jordanians, on the other hand, saw a drop in compressive strength when ash was added to Portland cement. Their paste strengths were much lower, peaking at 6530 PSI (45 MPa) for pure Portland cement paste at 28 days at a water/cement ratio of 0.4 [15].

MECHANICAL PROPERTIES OF CONCRETE

Two sets of concrete forms were prepared for physical testing. The first set, a control sample, was prepared with the basic concrete recipe without fly-ash replacement, while the second set with 45% fly-ash replacement (fly ash from Sample Period 3), was prepared with the workability agent (12 oz per 100 lb cement + ash) mixed with the cement separately.

The 17-day compressive strength of the standard formulation was 4010 PSI, while that for the ash-containing formulation was 5050 PSI. The length change test (ASTM C157-86) showed that from Day One to Day Seven the average shrinkage was 0.0023 inches for ash-containing specimens, compared to 0.0133 inches for specimens of standard concrete.

The abrasion test (ASTM C944-80) was performed on six two-inch-high cylinders, cut from two six-inch-in-diameter cylinders. One cylinder was standard concrete and the other was fly ash-containing concrete. The cut surfaces were abraded. The results are:

Specimen	Loss by Abrasion (Gram)			Average Loss
X-1-1	0.7	0.5	0.6	0.60
X-1-2	0.5	0.5	0.6	0.53
X-1-3	0.8	0.9	1.0	0.90
X-15-1	0.7	0.8	0.8	0.77
X-15-2	1.0	1.1	1.3	1.13
X-15-3	0.9	0.8	0.8	0.83

The freeze/thaw (ASTM C666-84) and deicing tests (ASTM C672-84) were performed by CBUL, using test specimens prepared at the University of Pittsburgh. The freeze-thaw tests were confounded by poor coarse aggregate performance. The samples containing oil shale ash had less resistance to scaling than those containing no ash.

The Chinese report that, for pastes in which 35 to 40 percent of the Portland cement has been replaced by shale ashes, sulfate resistance increases by 166 percent and the bleeding ratio drops nearly to zero. Other physical properties of the oil shale-containing cements appear to the Chinese to be comparable to cements containing coal fly ash [12].

ZERO-SLUMP MATERIALS

Compressed/Autoclaved Ash/Lime Pastes

Three two-sample sets of short, compressed cylinders (2.5 inches in diameter and 2 inches high), using fly ash from Sample Period 7, were prepared by R. I. Lampus Company, a member of the National Precast Concrete Association (NPCA) from Springdale, Pennsylvania (a suburb of Pittsburgh). The specimens had the following formulations:

	Percentage		
Specimen ID Number	Lime	Ash	Ash + Sand
1	8	--	92
2	10	90	--
3	15	85	--

An optimum amount of water (10 percent based upon dry weight) was added for maximum compaction. The cylinders were autoclaved at the University of Pittsburgh for eight hours at 170 psi (350°F) to obtain calcium silicate bonding. The compressive strengths achieved were 1500, 2130 and 2870 PSI respectively.

Concrete Masonry Units

Eight sets of zero-slump concretes, similar in formulation to concrete masonry units, were prepared at the University of Pittsburgh, two of them containing oil shale combustion fly ash. In all cases, cylinders four inches high and two inches in diameter were fabricated and then allowed to set at room temperature in a humid environment for five hours. Next, they were heated to 150°F at one atmosphere with steam over a two-hour period and then cured at 150°F and one atmosphere for twelve hours within a steamed environment before being cooled to room temperature.

The first set of four cylinders was prepared with fly ash partially substituting for Portland cement. The following formulation was used:

- 1119.8 grams sand;
- 136.9 grams Portland cement (Type 1);
- 63.0 grams oil shale fly ash;
- 49.3 grams water.

The particle size distribution of the sand was adjusted to an optimal one by screening and blending. The final sand blend was 14 percent greater than 4 mesh, 20 percent in the range of 4 to 8 mesh, and 66 percent less than 8 mesh. The cylinders were formed by pressing the concrete into the molds, followed by ten seconds of vibration at 900 CPM with a handheld unit. Release from the molds was difficult and the average compressive strength of the final product was very poor. The molds were oiled for future tests to make release more easily accomplished.

The second, third, fourth, fifth and sixth sets of four cylinders each (twenty in all) were made without fly ash substitution. Their purpose was to test various formulations and preparation techniques. An air entrainer was added for the fourth and fifth tests. For the sixth set the sand particle size distribution was set by screening and blending, according to the method suggested in the Technical Bulletin No. 5 of the National Concrete Masonry Association. All twenty cylinders were rodded, rather than vibrated. The oversized, handheld vibrator, used for the first set, tended to eject portions of the mix from the cylinders. The maximum compressive strengths of these cylinders after curing was 2000 PSI. It should be noted that the three-day strength of commercial concrete block is between 2000 and 2400 PSI.

The seventh and eighth sets of four cylinders each were prepared with 1344 grams sand, 150 grams water and either 240 grams Type 1 Portland cement (seventh set) or 168 grams Type 1 Portland cement and 72 grams oil shale fly ash (eighth set). The average compressive strength of the vibrated, cured cylinders was 1590 PSI for both sets.

Light-Weight Concrete

The third, and final, zero-slump product line that was examined was light-weight concrete. This material generally has a very low density (down to 25 lb/cubic foot) and a correspondingly low compressive strength (down to 60 PSI). It is used for fireproofing and insulation in structures. The "foaming approach" to produce this material, applied in this project, uses a foaming agent in the concrete mix. The agent introduces and stabilizes air bubbles during mixing at high speed. A sample of oil shale ash was provided to Elastizell Corporation of America in Ann Arbor, Michigan. A test using 60 percent Type 1 Portland cement and 40 percent oil shale ash yielded a well-mixing, quick-setting formulation, which resulted in a hard, strippable product in one day. The cast density of the sample was 40.3 lb/ft^3. Elastizell concluded that, based upon this limited investigation, oil shale combustion fly ash is a viable addition to light-weight concrete mixes.

CONCLUSIONS

The literature survey, conducted within the framework of this project, identified fifteen articles on the use of oil shale combustion ash in cement. These come from Israel, China, Jordan and the (former) USSR.

The ash from the combustor tests with 54 percent shale/46 percent coal is moderate in both CaO and MgO. The MgO is bound inside the particles and does not negatively impact the soundness of the ash.

Standard concrete with 15 percent substitution of Portland cement with ash shows an improvement in compressive strength at the same consistency (slump) of the wet mix, as standard Portland cement concrete. The addition of a wettability agent allows an additional 30 percent replacement without a drop in compressive strength below that of standard Portland cement concrete.

A first exploratory set of four physical tests were applied to the concrete which had 45 percent of the Portland cement replaced by ash, along with the addition of a wettability agent.

Preliminary specimens of three zero-slump products were prepared -- compressed/autoclaved ash/lime paste, concrete masonry units and light-weight concrete. The properties of the first product were sufficiently interesting that one manufacturer entered into direct negotiations with Occidental Oil Shale Company to test this product further. The second and third products met or exceeded one or more basic minimum standards, the third sufficiently so that one manufacturer desired to continue further testing. It is regrettable that Occidental Oil Shale Company has ceased operation, thus halting work in this promising area.

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REFERENCES

[1] Wuhrer, J., Zement-Kalk-Gips, April 1949, Pages 61-65, 89-93.
[2] Wuhrer, J., Zement-Kalk-Gips, March 1950, Pages 45-48.
[3] Rohrbach, R., Zement-Kalk-Gips, 22 (7), 1969, Pages 293-296.
[4] Rechneier, H., Zement-Kalk-Gips, 23 (6), 1970, Pages 249-253.
[5] Rapp, G., Betonwerk + Fertigteil-Technik, 50 (7), 1984, Pages 468-473.
[6] Mathauer, W., Betonwerk + Fertigteil-Technik, 50 (9), 1984, Pages 613-619.
[7] Puzyrev, Yu. A., Tekhnol. Izgot. i Svoistvanov. Kompozits. Stroit. Mater., L., 1986, Pages 63-68. Referenced in Ref. Zh., Khim. 1987, Abstr. No. 7M415.
[8] Remnev, V. A., Issled. po Str-vu Stroit. Teplofiz. Dolgovech. Konstruktsii, Tallin, 1987, Pages 75-85. Referenced in Ref. Zh., Khim. 1988, Abstr. No. 8P95.
[9] Puzyrev, Yu. A., A. B. Klyuev and I. I. Zinchenko, Intensif. Tekhnol. Protsessov v Pr-ve Sbor. Zhelezobetona, L., 1988, Pages 92-97. Referenced in Ref. Zh., Khim. 1989, Abstr. No. 11M340.
[10] Bentur, A., et al., Proceedings of the Second International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Madrid, Spain, April 21-25, 1986, SP 91-37, American Concrete Institute, Pages 779-802.
[11] Guangshu, T., et al., Proceedings of the International Conference on Oil Shale and Shale Oil, Colorado School of Mines 21st Oil Shale Symposium, Beijing, China, May 16-19, 1988, Pages 547-551.
[12] Zhongpu, H., and X. Qihai, Document of Reference 11, Pages 552-558.
[13] Guangshu, T., et al., Document of Reference 11, Pages 559-564.
[14] Zhimin, Wang, et al., Document of Reference 11, Pages 565-572.
[15] Smadi, M., A. Yeginobal, and T. Khedaywi, Magazine of Concrete Research, 41 (148), September 1989, Pages 183-190.